

# The Dynamic Nature of Hydridosilsesquioxane Clusters

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Beamline(s): U8B and U4IR

**Introduction:** Progress in the area of microelectronic device packing density, speed, and functionality generally requires smaller device dimensions.<sup>1</sup> The ensuing problems associated with smaller line dimensions such as propagation delay, cross-talk noise, and power dissipation must be addressed. As a solution to these issues, new low dielectric constant ( $k < 3$ ) materials have been proposed to replace the current Al(Cu) and SiO<sub>2</sub> interconnect technology. Hydridosilsesquioxane (HSQ) resin is a promising alternative consisting primarily of O<sub>3</sub>-SiH entities. However, device failure results when the polymer is employed in direct contact with the metal lines. To investigate the chemistry behind this, we have examined the interaction of HSQ clusters (HSiO<sub>1.5</sub>)<sub>n</sub> with gold surfaces. HSQ clusters such as H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> (**1**) and H<sub>10</sub>Si<sub>10</sub>O<sub>15</sub> (**2**) are volatile, well-defined species that can be considered monodispersed forms of the polymerized resin. The clusters form single Au-Si bonds in UHV conditions permitting high-resolution soft X-Ray photoemission (XPS) and reflection-absorption infrared spectroscopy (RAIRS) experiments. Coverage-dependent XPS and RAIRS data suggest surface equilibrium operative at all coverage regimes which involves facile making and breaking of Si-H bonds.

**Methods and Materials:** Both **1** and **2** were synthesized by the method of Agaskar and sublimed twice.<sup>2</sup> Gold samples were prepared by evaporating chromium or titanium onto SiO<sub>2</sub>/Si(100)-2x1 as an adhesive layer followed by at least 100 nm of gold. The sample purity was assessed by XPS. Monochromatic synchrotron XPS spectra were collected at U8b with an incident photon energy of 160 eV. The low frequency data was also obtained at NSLS at U4IR using a helium-cooled Cu-Ge detector.<sup>3</sup> Matlab Version 4.0 was employed for curve-fitting the photoemission data. The conventional RAIRS (for 750-3000 cm<sup>-1</sup> data) and XPS (for O1s characterization) are located at the University of Michigan and have been described elsewhere.<sup>4</sup>

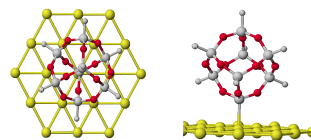
**Results:** Exposure of an evaporated gold surface to a saturating dose of **1** or **2** results in a chemisorbed monolayer on the gold surface. XPS and RAIRS data are consistent with the clusters bonding to the surface by a single vertex as illustrated in **Figure 1**. The XPS spectrum for **1** reveals two Si 2p<sub>3/2</sub> core-level features with binding energies -101.1 and -102.3 eV. The area ratio is 1:7.3 (**Figure 2**). The peak positions and area ratios remain constant for all coverage regimes. Similar data have been obtained for **2** at saturation coverage; however, the area ratio changes as a function of coverage from 1:5.4 at ~ 18% saturation to ~ 1:9 at full coverage while the peak positions remain constant. This surprising result implies that some of the clusters, at low coverage, may be bonded to the gold surface by two vertexes while others are bound by only a single vertex. At saturation coverage, the clusters initially bonded by two vertexes may have reacted with a hydrogen radical that results from the chemisorption of HSQ clusters, and remain bonded by only one vertex. Alternatively, those clusters have desorbed and been replaced by other single-vertex clusters. As coverage increases, more space constraints from neighboring clusters would be expected, reducing the number of correctly spaced double Si-H activation sites on the gold surface. This may eventually require the clusters to bond by a single-vertex at higher coverage. In summary, these data imply Si-H bonds can be formed and broken quite easily at and near the metal/oxide interface in the presence of hydrogen radicals.

**Conclusions:** XPS and RAIRS data indicate both **1** and **2** have a single-vertex bonding geometry on gold at saturation coverage. However, the dramatic differences observed as a function of coverage for **1** and **2** only provide a hint of the complexity to be expected for the actual HSQ resin/gold interface. An equilibrium, where chemical bonds are constantly broken and created, may be of importance during the early stages of device formation and operation.

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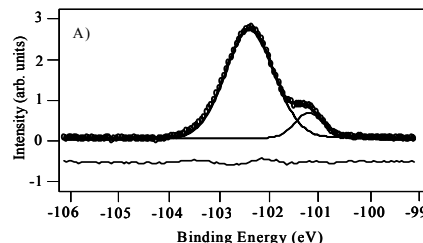
**References:** 1) W.W. Lee, P. S. Ho, *Mater. Res. Soc. Bull.*, **22**, 19, 1997. 2) P.A. Agaskar, *Inorg. Chem.*, **30**, 2707, 1991. 3) G.L. Carr, P. Dumas, C.J. Hirschmugl, G.P. Williams, *Nuovo Cimento* **20**, 375, 1998. 4) J.N. Greeley, L.M. Meeuwenberg, M.M. Banaszak Holl, *J. Am. Chem. Soc.*, **120**, 7777, 1998.

Figure 1:



**Figure 1.** Proposed structure of H<sub>7</sub>Si<sub>8</sub>O<sub>12</sub> on the gold surface. The orientation of the cluster is based upon a mechanics minimization of the H<sub>7</sub>Si<sub>8</sub>O<sub>12</sub> on an Au(111) crystal face.

Figure 2:



**Figure 2.** Soft X-ray Si 2p<sub>3/2</sub> core-level spectrum after the chemisorption of H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> to freshly evaporated gold.